MUTUAL DIFFUSION COEFFICIENTS OF SOME BINARY LIQUID SYSTEMS: TOLUENE-*n*-ALKYL ALCOHOL

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Experimental determinations of the mutual diffusion coefficients for binary systems of toluene-*n*-alkyl alcohol are reported here. The alcohols used were the first eight members of the homologous series of normal paraffinic alcohols.

1. Experimental

A diaphragm cell method²⁾ was used to measure the integral diffusion coefficients. A description of the experimental set-up and details of the experimental procedure are given in an earlier paper¹⁾ henceforth referred to as paper I. The equation used to calculate the integral diffusion coefficient is

$$D_{AB} = \frac{1}{\beta t} \ln \frac{C_{i,B} - C_{i,T}}{C_{f,B} - C_{f,T}} \quad (1)$$

The cell constant β was determined by diffusing 0.1 N potassium chloride solution into double-distilled water and obtaining the diffusion coefficient, D_{AB} , to be used in equation 1, from

$$D_{AB} = \frac{C_B D_{C,B} - C_T D_{C,T}}{C_B - C_T} \quad (2)$$

where

$$C_B = \frac{1}{2} (C_{i,B} + C_{f,B}) \quad (3)$$

and

$$C_T = \frac{1}{2} (C_{i,T} + C_{f,T}) \quad (4)$$

The parameter $D_{C,B}$, is the integral diffusion coefficient obtained in a run of vanishingly short duration with initial concentrations C_B and zero in bottom and top sides of the diaphragm, respectively. Similarly, $D_{C,T}$, is defined for the initial concentrations zero and C_T . The values of $D_{C,B}$ and $D_{C,T}$ were obtained from the literature³⁾.

As described in paper I, the cell constant β was measured after every 240 hours of usage. The value of β increased by 2.5% from its initial value of 1917.9 m^{-2} after 960 hours of usage.

All chemicals used were analytical reagent grade. The method of composition analysis is given in paper I.

Each diffusion run, lasting for 24 hours, was done in a thermostat kept at $28 \pm 0.5^\circ\text{C}$.

2. Results

Table 1 lists the density, refractive index and viscosity of the pure components used in this study as well as those given in the literature. **Table 2** gives the experimental diffusion coefficients at various compositions. Each datum is an average of three runs. As described in paper I, the error analysis showed that the maximum possible error in the diffusion coefficient, D_{AB} , could be 14%. No data for these systems are available in the literature.

3. Correlation

The diffusion coefficient data for all compositions of any binary system under study were fitted in the generalized expression

$$(D_{AB})_i = (1/2)k_{1i} + k_{2i}\bar{x}_A + k_{3i} \cos(2 \cos^{-1} \bar{x}_A) + k_{4i} \cos(3 \cos^{-1} \bar{x}_A) \quad (5)$$

where $(D_{AB})_i$ is the diffusion coefficient of the *i*th binary system, k_{1i} etc. are adjustable constants for the *i*th system, and $\bar{x}_A = 2x_A - 1.0$, where x_A is the mole fraction of toluene. Each of the four constants k_1 , k_2 , k_3 and k_4 thus obtained, was linearly correlated with a property, P , which is defined as

$$P = [M_A^{0.5} + \left(\frac{\eta_B}{\eta_A}\right)^{0.6}] / [\eta_A + \left(\frac{V_B}{V_A}\right)^{0.6}] \quad (6)$$

where M_A is the molecular weight of the solvent toluene and η_A , η_B , V_A and V_B are the viscosities and molar volumes of toluene and alcohol, respectively.

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Table 1

Chemical	Purity	Density at 20°C in gcm^{-3}		Refractive index at 20°C		Viscosity kg/m sec
		literature*	measured	literature*	measured	
Toluene	99.0	0.8670	0.8670	1.4970	1.4970	0.612
Methanol	99.8	0.7917	0.7918	1.3312	1.3313	0.652
Ethanol	—	0.7893	0.8019	1.3624	1.3639	1.484
<i>n</i> -Propanol	99.00	0.8044	0.8040	1.3854	1.3848	2.176
<i>n</i> -Butanol	99.00	0.8098	0.8120	1.3993	1.4000	2.907
<i>n</i> -Pentanol	99.00	0.8144	0.8145	1.4099	1.4102	3.931
<i>n</i> -Hexanol	99.00	0.8166	0.8187	1.4179	1.4183	5.061
<i>n</i> -Heptanol	99.00	0.8219	0.8233	1.4241	1.4249	6.616
<i>n</i> -Octanol	99.00	0.8246	0.8233	1.4292	1.4293	8.397
Potassium chloride	99.5					
Silver nitrate	99.5					

* Handbook of Chemistry and Physics, 58th Edition, CRC Press, Cleveland (1978)

Table 2. Integral Diffusion Coefficient at 28°C

Sl. No.	System	Mole fraction of toluene	Diffusion coefficient $\times 10^9 \text{m}^2/\text{sec}$	
			Experimental	Calculated eqn.7
1.	Toluene-Methanol	0.0000	1.374	1.382
		0.0955	1.264	1.274
		0.2036	1.185	1.186
		0.3744	1.170	1.141
		0.6180	1.364	1.332
2.	Toluene-Ethanol	0.0000	1.314	1.286
		0.1191	1.167	1.171
		0.2667	1.059	1.074
		0.4561	1.057	1.074
		0.6912	1.330	1.364
3.	Toluene-Propanol	0.0000	1.214	1.182
		0.1677	1.077	1.046
		0.3294	1.003	0.964
		0.5257	1.013	1.015
		0.7516	1.387	1.409
4.	Toluene- <i>n</i> -Butanol	0.0000	1.057	1.082
		0.2009	0.928	0.942
		0.3828	0.875	0.866
		0.5851	0.992	0.974
		0.7734	1.375	1.383
5.	Toluene- <i>n</i> -Pentanol	0.0000	0.919	0.968
		0.2222	0.789	0.834
		0.4201	0.713	0.758
		0.6044	0.854	0.883
		0.7924	1.346	1.349
6.	Toluene- <i>n</i> -Hexanol	0.0000	0.871	0.859
		0.2356	0.709	0.736
		0.4174	0.626	0.655
		0.6501	0.823	0.846
		0.8250	1.391	1.392
7.	Toluene- <i>n</i> -Heptanol	0.0000	0.733	0.750
		0.2313	0.641	0.648
		0.4602	0.568	0.550
		0.6669	0.780	0.769
		0.8699	1.511	1.441
8.	Toluene- <i>n</i> -Octanol	0.0000	0.658	0.641
		0.3127	0.531	0.499
		0.5288	0.479	0.463
		0.6912	0.724	0.717
		0.8154	1.357	1.363

The final generalized correlation of the diffusion coefficient with the property, P , for all the binary systems of toluene-alcohol is given by

$$D_{AB} \times 10^5 = 1.7078 - 0.0463 P [1 - 0.3946 \bar{x}_A] \\ + 0.4372 \bar{x}_A \\ + [0.0155 P + 0.3071] \cos[2 \cos^{-1} \bar{x}_A] \\ + [0.0121 P - 0.0059] \cos[3 \cos^{-1} \bar{x}_A] \quad (7)$$

The correlated data, given in Table 2, show good agreement with the experimental data, with an average deviation of about 2.3%.

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Nomenclature

$C_{i,B}, C_{i,T}$	= initial concentration of solvent (toluene) in the bottom and top compartments, respectively	$[\text{mol} \cdot \text{m}^{-3}]$
$C_{f,B}, C_{f,T}$	= final concentration of solvent (toluene) in the bottom and top compartments, respectively	$[\text{mol} \cdot \text{m}^{-3}]$
D_{AB}	= mutual diffusion coefficient when A	

$D_{C,B}, D_{C,T}$	= diffuses into B or vice versa integral diffusion coefficient in a vanishingly short duration which initial concentrations being C_B in the bottom compartment and zero in the top compartment, or C_T in the top and zero in the bottom compartment, respectively	$[\text{m}^2 \cdot \text{s}^{-1}]$
$(D_{AB})_i$	= diffusion coefficient in the i th binary system	$[\text{m}^2 \cdot \text{s}^{-1}]$
$k_{1i}, k_{2i}, k_{3i}, k_{4i}$	= constants in eqn. 1 for the i th binary system	$[\text{m}^2 \cdot \text{s}^{-1}]$
M_A	= molecular weight of solvent (toluene)	$[-]$
V_A, V_B	= molar volumes of solvent (toluene) and alcohol used in the binary system, respectively	$[\text{m}^3/\text{mol}]$
x_A	= mole fraction of solvent (toluene)	$[-]$
β	= cell constant	$[\text{m}^{-2}]$
η_A, η_B	= viscosities of toluene and alcohol used in the binary system, respectively	$[\text{kg m}^{-1} \text{s}^{-1}]$

Literature Cited

- 1) Ramprasad, G., T. R. Das and A. K. Mukherjee: *J. Chem. Eng. Japan*, **23**, 443 (1990).
- 2) Stokes, R. H.: *J. Am. Chem. Soc.* **72**, 763 (1950).
- 3) Woolf, L. A. and J. F. Tilley: *J. Phys. Chem.* **71**, 1962 (1967).